SEA WATER CONVERSION LABORATORY

UNIVERSITY OF CALIFORNIA

BERKELEY, CALIFORNIA



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Quarterly Report No. 9

April 15, 1970

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D. A. Zelman
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Contract No. 952109
Jet Propulsion Laboratory
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## ABSTRACT, CONCLUSIONS AND RECOMMENDATIONS

This report describes the measurement of diffusive and electrical transport of KOH and dissolved ZnO through the JPL 119 GX membrane bounded by concentrated KOH solution. The following measurements were performed:

a) Diffusive transport of KOH and water; membrane bounded by 5M and 1M KOH.

b) Electrical transference of $K^+$ (or $OH^-$) and water; membrane bounded by 5M KOH.

c) Diffusive transport of ZnO dissolved in 5M KOH.

The mass transfer coefficient of KOH was found to be $(6.7 \pm 0.3) \times 10^{-4}$ cm $sec^{-1}$, the $K^+$ transport number $0.38 \pm 0.02$. The mass transfer coefficient found for the Zn species was $(6.7 \pm 0.2) \times 10^{-5}$ cm $sec^{-1}$. The Zn mass transfer coefficient was determined from the total zinc transfer; no assumptions concerning the composition of the actual Zn ions or complex ions present are necessary. The membrane was found to be slightly cation-selective, even with the concentrated KOH solutions used as bounding solutions.

Electrical transference experiments with KOH solutions containing ZnO and bounding the membrane are in progress and will be described in a forthcoming progress report.

## LIST OF SYMBOLS

| | |
|---|---|
| $A$ | exposed membrane area ($cm^2$) |
| $B$ | concentration parameter defined by Eq. (7) ($sec^{-1}$) |
| $C_{s,o}$ | solute concentration at $t = 0$ (mole $cm^{-3}$) |
| $C_{s,t}$ | solute concentration at time t (mole $cm^{-3}$) |
| $\Delta C_s$ | concentration difference between two bounding solutions, $c_s' - c_s''$ (mole $cm^{-3}$) |
| $d$ | thickness (cm) |
| $I$ | electric current (Amp) |
| $K_s$ | solute mass transfer coefficient (cm $sec^{-1}$) |
| $K_w$ | volume transfer coefficient ($cm^4$ $mole^{-1}$ $sec^{-1}$) |
| $m$ | molality |
| $n_{s,o}$ | total number of moles of solute in half-cell at $t = 0$ |
| $n_{s,t}$ | total number of moles of solute in half-cell at time t |
| $\delta n_{s,t}$ | change in total number of moles of solute in half-cell |
| $t$ | time (sec) |
| $\delta t$ | time elapsed between two sampling in diffusion experiment (sec) |
| $t_+$ | transport number of the positive ion in the solution |
| $\bar{t}_+$ | transport number of the positive ion inside the membrane |
| $\bar{t}_w$ | water transport number inside the membrane |
| $V_o$ | solution volume at $t = 0$ ($cm^3$) |
| $V_t$ | solution volume at time t ($cm^3$) |
| $\delta V_t$ | change in solution volume, $V_o - V_t$ ($cm^3$) |
| $\bar{v}$ | partial molal volume ($cm^3$ $mole^{-1}$) |
| $\mathcal{F}$ | Faraday's constant |
| $\delta$ | difference in time |

List of Symbols (continued)

| | |
|---|---|
| $\Delta$ | difference between two bounding solution, ' - '' |
| $\phi$ | apparent molal volume ($cm^3$ $mole^{-1}$) |
| $\rho$ | density (gram $cm^{-3}$) |

## I. Introduction

The research effort in the period covered by this report can be divided into two parts.

The first part is the continuation of the research program designed to test an apparatus for the measurement of the transport of salt, ions and water across membranes, with differences in concentration, electric potential and pressure as driving forces. The complete experimental system was described in detail in the eighth quarterly report (January 15, 1970). At the moment this system is being applied to ion-exchange membranes in contact with NaCl solutions of 0.5M or lower, but the system is also very suitable for the study of neutral and more porous membranes in contact with salt solutions.

The second part of the research effort was directed towards the study of transport properties of membranes bounded by concentrated KOH solutions. In its present form the "concentration clamp" system mentioned above cannot be used in these solutions. It was decided to perform the transport measurements in the concentrated KOH solutions using a conventional quasi-steady state system in a transport cell made of Pyrex glass. The membrane used was supplied by the Jet Propulsion Laboratory (119GX). This membrane has a polyethylene base which is grafted with acrylic acid and cross-linked with divinylbenzene. Membrane potential measurements with dilute NaCl solutions as bounding solutions showed the membrane to be moderately cation-selective in a 0.1M NaCl solution.

In this quarterly report we discuss the measurements with the Jet Propulsion Laboratory 119GX membrane in concentrated KOH solutions with and without dissolved ZnO. The progress with the "concentration clamp" system will be described in the next report.

## II. Experimental

### II.1 Experimental Apparatus

A transport cell made of Pyrex glass was assembled to perform diffusion and electromigration measurements across membranes in contact with concentrated KOH solutions. Pyrex glass showed good long-term resistance against concentrated KOH solutions at ambient temperature. The cell consists of two P8320 thick-wall 90° Pyrex elbows (Conical pipe, Corning Glassworks, Blacksburg, Virginia), 1" i.d., clamped together with the membrane holder in between. The membrane holder consists of two plates of G-11 fiberglass-reinforced epoxy, 1/16" thick, (Synthane Corporation, Oaks, Pennsylvania), with a 3/8" diameter hole in the middle leaving an active membrane area of 0.73 $cm^2$. The membrane is clamped between these two plates; there is an O-ring seal between each glass elbow and the membrane holder. The vertical part of the elbow is closed with a rubber stopper to prevent evaporation, although a pinhole in the stopper prevents pressure-buildup.

In electromigration experiments Pt electrodes are fitted in the rubber stopper. Normally each half-cell is filled with 50 $cm^3$ solution. In the electromigration experiments a CK40-0.8M automatic cross-over power supply (Kepco Inc., Flushing, New York) was used in the constant-current mode. A 10 Ohm Standard resistor was connected in series with The cell. The voltage drop across this resistor was measured using a K-5 potentiometer (Leeds and Northrup, North Wales, Pennsylvania), from which the current could be calculated accurately. Blank Pt electrodes were used for anode and cathode.

In all experiments the solutions are stirred with magnetic stirring bars inside the half-cell, at approximately 200 rpm. The stirring

is probably not sufficient to completely eliminate the mass transfer resistance of the membrane-solution boundary layer. Its main purpose is to mix the solutions in the half-cells during and directly after the experiment.

The following transport experiments have been carried out in this cell, using the Jet Propulsion Laboratory 119GX membrane to separate the two cell compartments:

a) Diffusion of KOH. Initial bounding solutions were approximately 5.0 and 1.0M KOH, final concentrations approximately 4.5 and 1.5M. The total water transport (osmotic flow) could also be determined, although not very accurately.

b) Electrical transport measurements in approximately 5.0M KOH solutions. Pt electrodes were used, total currents of around 150 mA were applied. The transport number of the $K^+$ ion can be calculated fairly accurately, the transport number of the water (moles of water transported per Faraday of charge passed through the membrane) is obtained with moderate accuracy.

c) Diffusion of Zn species from a solution approximately 5M in KOH + 0.1M in ZnO through the membrane to a 5M KOH solution containing no ZnO. A total Zn concentration change of 0.016M occurred during the experiment.

Electrical transport measurements with 5M KOH + 0.1M ZnO bounding solutions are in progress and will be described in a forthcoming progress report.

## II.2. Chemicals and Analytical Determinations

KOH and ZnO were "Reagent Grade" (Mallinckrodt Chemical Works,

St. Louis, Missouri). They were used without further purification. Deionized and deaerated water was used to make the required solutions. The solutions were kept in well-stoppered polyethylene bottles, but no special precautions were taken to prevent $CO_2$-uptake during storage, transfer and experiment. $OH^-$ concentrations of the experimental solutions were always redetermined shortly before an experiment, but in no case did we find significant changes due to $CO_2$-uptake. The presence of a relatively small amount of carbonate ions would not interfere with our transport measurements. KOH concentrations were determined by titration with standard HCl solutions using phenolphtalein indicator. In KOH solutions containing ZnO the titration was ended when the solution was colorless. A $Zn(OH)_2$ precipitate remained; the pH of the final solution was found to be around 7. Thus only the "free" $OH^-$ was determined and $Zn(OH)_2$ remained as a precipitate. Zn concentrations were determined by first neutralizing the solution sample with 1M or 5M HCl and subsequent titration with E.D.T.A. using a PH 10 buffer and Eriochrome Black as indicator. Accuracy of the concentration determinations is extremely important because of the relatively small concentration changes that have to be detected. Repeatability of the $OH^-$ determinations is estimated at 0.1% when no Zn is present in the solution and at 0.1 - 0.2% for solutions containing ZnO. Repeatability of Zn determinations, using a 0.01N E.D.T.A. solution, was better than 0.2% when more than 10 ml E.D.T.A. was used but this uncertainty became proportionally higher when smaller quantities of E.D.T.A. were needed.

## II.3 Experimental Procedure and Calculations

In a KOH diffusion experiment 50 ml of solution of known KOH

concentration is pipetted into each half-cell; solutions approximately 5M and 1M in KOH were used in each half-cell respectively. Transport of solute and of water through the membrane is allowed to take place for a certain period of time, $\delta t$, ranging from 2 to 4 hours. Then a 2 ml solution sample is taken from each compartment and the KOH concentration is determined. The remaining solution in each compartment is transferred completely to a volumetric flask and the total number of moles of KOH in each compartment is determined by titrating an aliquot. The final volume of the solution in each compartment was then calculated from the following equation:

$$V_t = n_{s,t} / C_{s,t}$$

$V_t$ is the final solution volume ($cm^3$), $n_{s,t}$ the total number of moles of KOH in the compartment at the time t, and $C_{s,t}$ the final KOH concentration. This method was used because the apparatus did not have provisions for <u>accurate</u> volume-change measurements. $\delta V_t = V_t - V_o$ normally was 1 to 2 ml. In all experiments $\delta V_t'$ and $\delta V_t''$, the volume changes of the more concentrated solution (') and the more dilute solution ('') respectively, corresponded to each other within measurement error; however, this measurement error could be appreciable due to the relatively small difference between $V_t$ and $V_o$, resulting in only approximate values for the water transfer coefficient $K_w$. The total solute transport, $\delta n_{s,t}$ (moles) is given by:

$$\delta n_{s,t} = V_o \cdot C_{s,o} - n_{s,t}$$

where $V_o$ is the solution volume at t = 0 ($cm^3$), $C_{s,o}$ the KOH concentration at t = 0 ($mole/cm^3$) and $n_{s,t}$ the final total number of moles of KOH after time t. In all experiments the difference between $\delta n_s'$ and $\delta n_s''$ was within measurement error.

In a diffusion experiment the concentration difference between the solutions bounding the membrane decreases with time and hence $\delta n_{s,t}$ does vary linearly with t. At any time, t, the transport of solute, s, is given by:

$$-\frac{dn_s'}{dt} = +\frac{dn_s''}{dt} = K_s \cdot A(C_s' - C_s'') \qquad (1)$$

and the volume transport by:

$$\frac{dV'}{dt} = -\frac{dV''}{dt} = K_w \cdot A(C'_s - C''_s) \qquad (2)$$

In these equations ' denotes the more concentrated solution, '' the more dilute solution. $n_s$ is the number of moles of solute in a compartment, and V volume of the solution in a compartment ($cm^3$). A is the membrane area ($cm^2$), $C_s$ the solute concentration ($moles/cm^3$) and t the time (sec). $K_s$ is the solute transfer coefficient ($cm\ sec^{-1}$) and $K_w$ the coefficient describing the volume transport ($cm^4\ mole^{-1}\ sec^{-1}$). Equation (2) is not exact, since the volume is not a conserved quantity in the transport process, due to the differences of the partial molar volumes in the two solutions bounding the membrane. This difference between $\Delta V'$ and $\Delta V''$ is not large enough to be detected in our experiments and the use of Equation (2) is justified within the experimental limits of error.

Integration of Equations (1) and (2) gives:

$$- \delta n'_{s,t} = + \delta n''_{s,t} = K_s \cdot A \int_o^t (C'_s - C''_s)\, dt \qquad (3)$$

$$\delta V'_t = - \delta V''_t = K_w \cdot A \int_o^t (C'_s - C''_s)\, dt \qquad (4)$$

The time dependence of $(C'_s - C''_s)$ can be solved using Equations (1) and (2). Since $n = V.c$, Equation (1) yields:

$$- V' \frac{dc'_s}{dt} - C'_s \frac{dV'}{dt} = K_s \cdot A(C'_s - C''_s) \qquad (5)$$

$$+ V'' \frac{dc''_s}{dt} + C''_s \frac{dV''}{dt} = K_s \cdot A(C'_s - C''_s) \qquad (6)$$

Dividing (5) by $V'$, (6) by $V''$, adding the two resulting equations, substituting for $\frac{dV'}{dt} = - \frac{dV''}{dt}$ from Equation (2), and integration of the final equation obtained for $d(C'_s - C''_s)/dt$ yields the desired relation between $\Delta C_s$ $(=C'_s - C''_s)$ and t:

$$\Delta C_{s,t} = \Delta C_{s,o} \cdot \exp(-B.t) \qquad (7)$$

with

$$B = K_s \cdot A(\frac{1}{V'} + \frac{1}{V''}) + K_w \cdot A(\frac{C'_s}{V'} + \frac{C''_s}{V''}) \qquad (8)$$

In this derivation $(\frac{1}{V'} + \frac{1}{V''})$ and $(\frac{C'_s}{V'} + \frac{C''_s}{V''})$ are assumed to be independent

of time. This assumption is justified by the fact that the volume changes are small and that $V' \simeq V''$. Also $\delta C_s'$ is approximately equal to $\delta C_s''$. In our experiments this assumption is valid within experimental error. Using Equation (7) we can now solve Equations (3) and (4) to obtain expressions for $K_s$ and $K_w$:

$$K_s = - \frac{\delta n'_{s,t} \cdot [\ln \Delta C_{s,o} - \ln \Delta C_{s,t}]}{t \cdot A \cdot [\Delta C_{s,o} - \Delta C_{s,t}]} \tag{9}$$

$$K_w = \frac{V'_t \cdot [\ln \Delta C_{s,o} - \ln \Delta C_{s,t}]}{t \cdot A \cdot [\Delta C_{s,o} - \Delta C_{s,t}]} \tag{10}$$

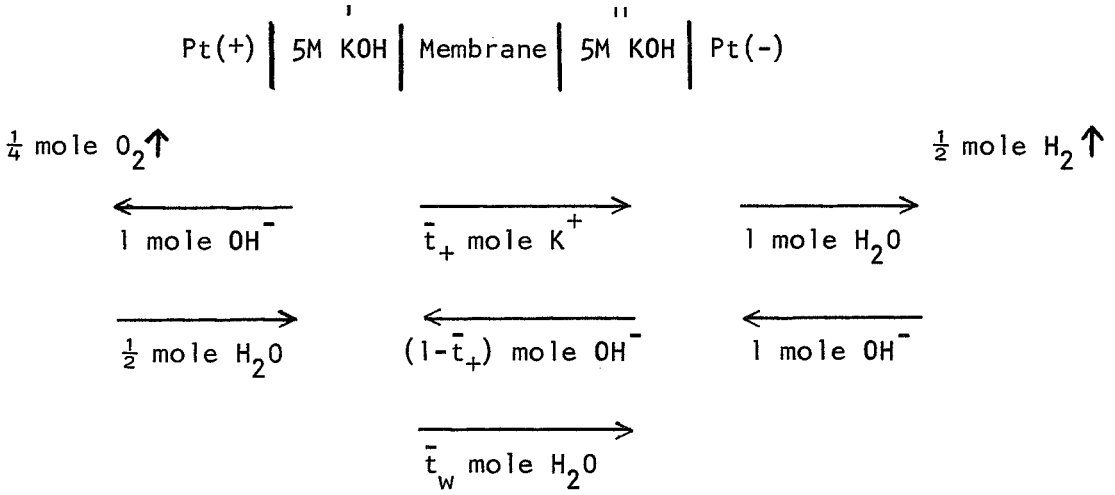
Thus we see that knowledge of $\delta n_s'$ (or $\delta n_s''$) only is not enough to calculate $K_s$ or $K_w$ in a system where the concentration are allowed to change considerably: both $\delta n_s$ and the concentrations have to be measured. Accurate measurement of the volume change during an experiment would also be sufficient, provided that the initial volume is known accurately.

In a Zn-diffusion experiment 50 ml of an approximately 5M KOH + 0.1M ZnO solution was pipetted into one half-cell and 50 ml of a 5.2M KOH solution was pipetted into the other. Without defining the Zn species which are actually present ($ZnO_2^{2-}$ or $Zn(OH)_4^{2-}$ or any other complex ions) we can measure the total amount of Zn being transferred through the membrane and calculate a Zn transfer coefficient $K_s(Zn)$ using Equation (1) or (9), and the Zn concentration for $C_s$. Water transport in these

experiments may be neglected because the difference in total solute activity between the two solutions is small. Solution samples of 2 ml were taken from each compartment at regular intervals and the Zn content of the samples was determined. Thus a plot of $\ln\Delta C_{s,o} - \ln\Delta C_{s,t}$ vs t can be made which should result in a straight line through zero (Equations 7 and 8). $K_w$ is effectively zero. Hence $K_s$ can be determined from the slope of this line.

A correction has to be made for the volume change of the solutions because of the sample taking. Instead of t a summation of $t \cdot (\frac{1}{V'} + \frac{1}{V''})$ should be used as abscissa. The slope of this line yields $K_s \cdot A \cdot$ (See Figure 1). When samples are taken, Equation (9) may not be used because of the decreasing solution volumes, which were not taken into account in the derivation.

In the <u>electrical transference experiments</u> 50 ml of an approximately 5M KOH solution were pipetted into each half-cell. Pt electrodes were used, resulting in the following overall transport process for each Faraday of charge passed:



Thus for each Faraday of charge passed, the left side (anode) compartment has a net loss of $\bar{t}_+$ moles of KOH and $(\bar{t}_w - \frac{1}{2})$ moles of water. The right side (cathode) compartment has a net gain of $\bar{t}_+$ moles of KOH and $(\bar{t}_w - 1)$ moles of water. When the back-diffusion effect is small (this is always the case in our experiments, as is explained below), the transport number of the positive ion, $\bar{t}_+$, in the membrane is calculated from:

$$\bar{t}_+ = \delta n_s \cdot \mathcal{F} / (I \cdot t)$$

$\delta n_s'$ and $\delta n_s''$ should be equal. When $\bar{t}_+$ is known, the water transport number $\bar{t}_w$ can be calculated from the volume change in each compartment:

$$\delta V_t' = - \frac{I}{\mathcal{F}} [\bar{t}_+ \cdot \bar{V}_{KOH} + \bar{V}_{H_2O} (\bar{t}_w - \tfrac{1}{2})] \cdot t \qquad (11)$$

for the anode compartment, and

$$\delta V_t'' = + \frac{I}{\mathcal{F}} [\bar{t}_+ \cdot \bar{V}_{KOH} + \bar{V}_{H_2O} (\bar{t}_w - 1)] \cdot t \qquad (12)$$

for the cathode compartment. $I$ is the total electric current (Amp), $\mathcal{F}$ the Faraday and $\bar{V}$ the partial molal volume ($cm^3$ mole-1). $\delta V_t'$ and $\delta V_t''$ should not be equal because of the volume effect of the electrode reaction, which takes away 1 mole of $H_2O$ from the cathode compartment and adds $\frac{1}{2}$ mole of $H_2O$ to the anode compartment per Faraday of charge passed. Because $\Delta V'$ and $\Delta V''$ are not known very accurately, the two sides may give values for $t_w$ that differ as much as 30%. For this reason we may use $\bar{V}_{H_2O} = 18$ $cm^3$/mole without introducing a significant error. Density data for concentrated KOH solutions were used to calculate $\bar{V}_{KOH}$ in these

systems, using the relation:

$$\bar{V}_{KOH} = m\frac{d\phi}{dm} + \phi \qquad (13)$$

where m is the molality and $\phi$ the <u>apparent</u> molal volume. $\phi$ is calculated from density data:

$$\phi = \frac{1000}{m}\left(\frac{1}{\rho} - \frac{1}{\rho_o}\right) + \frac{W}{\rho} \qquad (14)$$

(See e.g. G. N. Lewis, M. Randall, Thermodynamics, Second Edition, McGraw Hill, New York 1961, p. 203-209.)

$\rho_o$ is the density of pure water, $\rho$ the density of a m molal solution and W the molecular weight of the solute.

Between 1M and 7M KOH we found that the partial molal volume is accurately represented by:

$$\bar{V}_{KOH} = 6.239\ m^{\frac{1}{2}} + 2.622$$

Deviations at 1M and at 7M KOH are less than 1%, and this equation represents the data appreciably better than within 1% for molalities between 1M and 7M KOH.

During the electromigration experiment a concentration difference is building up between the two solutions bounding the membrane. Thus back-diffusion of KOH may occur, which has the effect to lower the measured transport number of $K^+$. Of course this back diffusion effect will be small when only small concentration differences are allowed to build up.

Suppose $\bar{t}_+$ is to be determined with an error not exceeding 2% (this means a 2% error in the determination of $\delta n_{s,t}$). The accuracy of the $OH^-$ concentration determination is as good as ± 0.1% and at the end of the experiment the concentration difference between the solutions does not have to exceed 10% of the original solution concentration.

The back-diffusion effect will be negligible when $K_s \cdot A \cdot (\frac{1}{V'} + \frac{1}{V''}) \cdot \Delta t$ is much smaller than unity, independent of the current density used. This requirement is normally met in all our experiments. Even when $K_s \cdot A \cdot (\frac{1}{V'} + \frac{1}{V''}) \cdot \Delta t$ is as large as 0.1, (i.e. for experimental times longer than 10 hours), using the $K_s$ obtained from KOH diffusion experiments, the error in $t_+$ caused by back-diffusion is only about 5%. In all our experiments the error caused by back-diffusion was never larger than 2%, i.e. the approximate error due to the analytical determinations.

## III. Results and Discussion

### III.1 Diffusion of KOH

In a typical diffusion experiment using the 119GX membrane between solutions of 5.157 and 1.031 mole/liter KOH the following results were obtained. Concentrations, c, are in moles/liter. $\Delta t = 14.4 \times 10^3$ sec, 4 hr, exposed membrane area, A= 0.73 $cm^2$

Compartment containing concentrated solution (')

$C'_{s,o} = 5.157 \pm 0.005$ $\quad V'_o = 49.87 \pm 0.05$ ml $\rightarrow$ $\quad n'_{s,o} = 257.2 \pm 0.5$ mmole

$C'_{s,t} = 4.639 \pm 0.008 \rightarrow \quad V'_t = 50.03 \pm 0.15$ ml $\leftarrow \quad n'_{s,t} = 232.1 \pm 0.3$ mmole

$\delta V'_t = + 0.16 \pm 0.20$ ml $\quad \delta n'_{s,t} = - 25.1 \pm 0.8$ mmole

Compartment containing dilute solution ('')

$C''_{s,o} = 1.031 \pm 0.001$ $\quad V''_o = 49.87 \pm 0.05$ ml $\rightarrow$ $n''_{s,o} = 51.42 \pm 0.10$ mmole

$C''_{s,t} = 1.559 \pm 0.002 \rightarrow V''_t = 49.53 \pm 0.12$ ml $\leftarrow n''_{s,t} = 77.21 \pm 0.12$ mmole

$\delta V''_t = -0.34 \pm 0.17$ ml $\quad \delta n''_{s,t} = +25.8 \pm 0.2$ mmole

It is seen that the mass balance required for the KOH transport ($\delta n'_s = -\delta n''_s$) was satisfied within experimental error. The agreement for the volume flow, although within experimental error, is not good enough to allow anything more than an order of magnitude calculation of $K_w$. If we use the average of $\delta n'_s$ and $\delta n''_s$, $n_s = 25.5 \pm 0.4$ mmole and assume the limit of error in the estimate of the membrane area, A, to be 2%, we find:

$$K_s = (6.7 \pm 0.3) \times 10^{-4} \text{ cm sec}^{-1}$$

For $K_w$ we find the approximate value:

$$K_w = (7 \pm 3) \times 10^{-6} \text{ cm}^4 \text{ mole}^{-1} \text{ sec}^{-1}$$

Accurate measurements of $K_w$ would require a volume-measurement technique rather than the calculation of the final volume from the sample concentration and total amount of KOH, used here. It should be noted that the mass transfer coefficients $K_s$ and $K_w$ are dependent on the concentration. The dependence is believed to be sufficiently small to be negligible in practical battery separator work. Evaluation of this concentration dependence would require a large number of diffusion measurements using small concentration gradients. The values measured by us may be considered average values in the concentration region 1M - 5M KOH.

It is of interest to compare the mass transfer coefficient of KOH through the 119GX membrane with the value calculated for the case of free diffusion through a solution layer of the same thickness. Unfortunately no diffusion data for KOH could be found in a limited literature search. However, the variation in the diffusion coefficients of the potassium halides in aqueous solutions of 2-5 moles/liter is known to be less than 25% (R. A. Robinson, R. H. Stokes, Electrolyte Solutions, Butterworths, London 1959, p. 515) varying slightly between 2 and $2.5 \times 10^{-5}$ $cm^2$ $sec^{-1}$. If we assume a KOH diffusion coefficient in 3M solution of $2.5 \times 10^{-5}$ $cm^2$ $sec^{-1}$,* the corresponding mass transfer coefficient through a solution layer of thickness d would be $2.5 \times 10^{-5}/d$ cm $sec^{-1}$. We have no exact data for the thickness of the swollen 119GX membrane, but d is probably less than $10^{-2}$ cm. If we assume $d = 10^{-2}$ cm, $K_s$ (solution) would be $2.5 \times 10^{-3}$ cm $sec^{-1}$, or about 4 times the value found by us for the 119GX membrane. This ratio should be approximately the same for the electrical conductance of the membrane and a solution layer of the same thickness. (In this calculation the influence of the unstirred boundary layer next to the membrane is ignored. If the increased resistance of this boundary layer were taken into account, the resulting ratio between the membrane transfer coefficient and the solution transfer coefficient would be less than 4. We do not believe that the effect is large in the concentrated solutions examined here, however.)

### III.2 Electrical Transference Experiments

Four electrical transference experiments were made to determine the transport number of the positive ion and the water transport number when

*This estimate was made because primarily the less mobile ion (in this case probably $K^+$) determines the magnitude of the diffusion coefficient.

an electric current is passed through the 119GX membrane bounded by approximately 5M KOH solutions. The results for $t_+$ from the four experiments were in very reasonable agreement. The accuracy in $t_w$ is less, but the deviations between the last three experiments are within the expected limits of error. In the first exploratory experiment no reliable result for the volume flow was obtained. The experimental data for a typical electromigration experiment are given below. Concentrations are given in moles per liter of solution.

Run number 5

$\delta t = 2.10 \times 10^4$ sec  $A = 0.73 \pm 0.01$ cm$^2$  $I = 150.6 \pm 0.1$ mA

Anode compartment (')

$C'_{s,o} = 5.157 \pm 0.005$  $V'_o = 50.00 \pm 0.05$ ml $\rightarrow$ $n'_{s,o} = 257.8 \pm 0.5$ mmole

$C'_{s,t} = 5.003 \pm 0.010 \rightarrow$ $V'_t = 49.10 \pm 0.15$ ml $\leftarrow$ $n'_{s,t} = 245.7 \pm 0.3$ mmole

$\delta V'_t = -0.90 \pm 0.20$ ml  $\delta n'_{s,t} = -12.1 \pm 0.8$ mmole

Cathode compartment ('')

$C''_{s,o} = 5.157 \pm 0.005$  $V''_o = 50.00 \pm 0.05$ ml $\rightarrow$ $n''_{s,o} = 257.8 \pm 0.5$ mmole

$C''_{s,t} = 5.355 \pm 0.010 \rightarrow$ $V''_t = 50.50 \pm 0.15$ ml $\leftarrow$ $n''_{s,t} = 270.4 \pm 0.3$ mmole

$\delta V''_t = +0.50 \pm 0.20$ ml  $\delta n''_{s,t} = +12.6 \pm 0.8$ mmole

The agreement between $\delta n'$ and $\delta n''$ is well within the limits of error. From the average value we obtain for the transport number of the potassium ion:

$$\bar{t}_+ = 0.377 \pm 0.009$$

Using Equations (11) and (12) to calculate the water transport number $\bar{t}_w$, we find:

$$\text{from } \delta V': \quad \bar{t}_w = +1.7 \pm 0.3$$

$$\text{from } \delta V'': \quad \bar{t}_w = +1.5 \pm 0.6$$

The agreement between these values is also well within the maximum limits of error. It should be noted that the agreement between the two water transport numbers is better than the agreement between $\delta V'$ and $\delta V''$, because of the different volume correction for the electrode reaction in the two compartments.

In the three other experiments the following values for $\bar{t}_+$ were obtained (all values are calculated from the averages of the data for the anode and for the cathode compartment): $0.39 \pm 0.07$ (first exploratory experiment), $0.40 \pm 0.02$, $0.37 \pm 0.01$.

The average value of the $K^+$ transport number in the 119GX membrane bounded by a 5M KOH solution, calculated from these four experiments, is: $\bar{t}_{K^+} = 0.38 \pm 0.02$. From limiting equivalent conductances the transport number of $K^+$ in dilute aqueous solutions is found to be 0.27. In more concentrated solutions we would expect the transport number of $K^+$ to be slightly lower. Since $\bar{t}_{K^+}$ was found to be significantly higher than the latter value, the 119GX membrane has a preferential selectivity for $K^+$ ions over $OH^-$ ions when in contact with concentrated KOH solutions, although not a very pronounced one.

In a total of three experiments, we found for the water transport number $\bar{t}_w$: $+1.8 \pm 0.3$, $+1.6 + 0.3$ (the experiment described above) and $+1.7 \pm 0.2$. The positive sign means the net water transport is in the

direction of the positive current, i.e. with the $K^+$ ions, in spite of the higher transport number of $OH^-$. The average of these three values, $\bar{t}_w = + 1.7 \pm 0.2$, is probably fairly well established. More accurate estimates for $\bar{t}_w$ could be obtained if volume changes were recorded rather than calculating the final volume from the sample concentration and the total amount of KOH present, but the gas evolution at the electrodes would present some serious problems in the measurement of volume changes.

### III.3 Zn Diffusion

The diffusion of ZnO dissolved in approximately 5M KOH solution through a JPL 119GX membrane was measured by taking samples from the two compartments at regular time intervals and determining the Zn concentration. The way in which $K_s$ (Zn) can be calculated from these data was presented in Section II. In the actual experiment, one compartment (') was filled with 50.00 ml of a (4.970 ± 0.005) M KOH + (0.1009 ± 0.0001) M ZnO solution; the other compartment ('') was filled with 50.00 ml of a 5.157 ± 0.005 M KOH solution. Five 2.000 ± 0.002 ml samples were taken at regular intervals and the Zn concentrations determined. The total experiment lasted approximately 51 hours. The final Zn concentrations were 0.0841 ± 0.0001 M at the high concentration side and 0.0164 ± 0.0001 M at the low concentration side. The final $OH^-$ concentrations in the two compartments were equal (5.059 ± 0.005(') and 5.057 ± 0.005 M('') respectively) indicating that the KOH diffusion is much faster than the diffusion of the Zn species. The Zn mass balance was verified within ± 0.1%: $\delta n_{Zn}' = - 0.757$ mmole, $\delta n_{Zn}'' = + 0.758$ mmole. These figures were obtained by adding the number of mmoles of Zn in the samples to the total amount of Zn present in the final solution. For the KOH transport the figures

were: $\delta n_{OH}^{I} = 8.8$ mmole, $\delta n_{OH}^{II} = -6.1$ mmole. This agreement is also very satisfactory, taking into account that approximately 250 mmoles KOH are present in each compartment.

A graph showing $\ln\Delta C_{Zn,o} - \ln\Delta C_{Zn,t}$ vs. the sum of $\delta t(\frac{1}{V^I} + \frac{1}{V^{II}})$ for the different time intervals is shown in Figure 1. t is the total time elapsed, i.e. the sum of the times $\delta t$ in between two sample points. The term $(\frac{1}{V^I} + \frac{1}{V^{II}})$ is necessary to correct for the decrease in solution volume each time a solution sample is taken. $\delta t$ is the time elapsed between two sample points and $V^I$ and $V^{II}$ the volumes during that time interval. The summation is over $\delta t \cdot (\frac{1}{V^I} + \frac{1}{V^{II}})$ during the five intervals. From the slope of Figure 1 we obtain the mass transfer coefficient of the dissolved Zn species using the relation:

$$\ln\Delta C_{Zn,o} - \ln\Delta C_{Zn,t} = K_s \cdot A \cdot \Sigma\, \delta t \cdot (\frac{1}{V^I} + \frac{1}{V^{II}})$$

The result is:

$$K_s\ (Zn) = (6.7 \pm 0.2) \times 10^{-5}\ \text{cm sec}^{-1}$$

This mass transfer coefficient is about ten times smaller than the coefficient obtained for KOH diffusion. No data for the diffusion of Zn species in free KOH solutions are available. These data would be of interest to determine whether the membrane plays an <u>active</u> role in preventing the Zn species to diffuse from one electrode compartment to the other, i.e. if the membrane has transport specificity for KOH compared to the Zn species. Electrical transference experiments are now underway to predict the importance of Zn transport occuring at the time of <u>electrical</u> charging

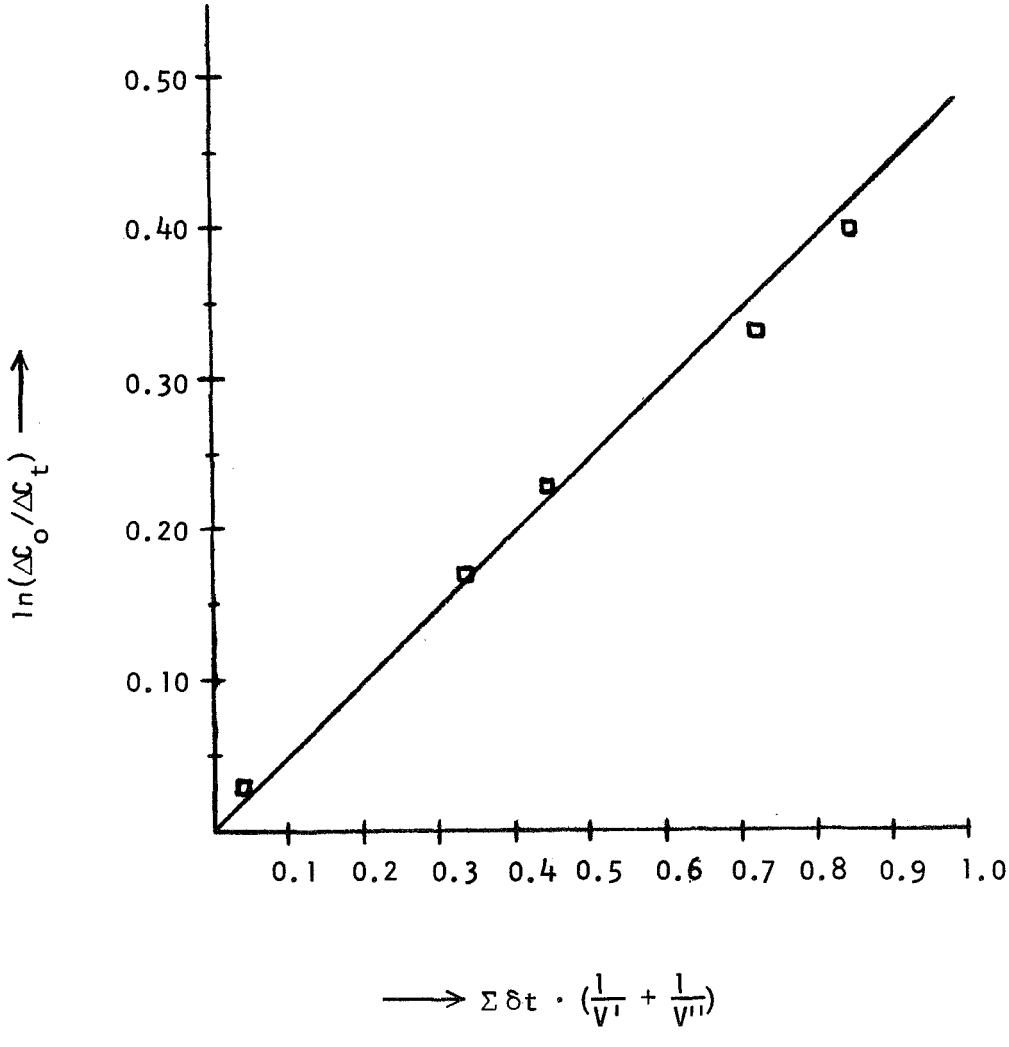



Figure 1. Diffusion of Zn across JPL 119GX membrane: logarithm of the concentration difference vs. time, $\delta t$, corrected for volume changes of the cell solution.

or discharging of a battery relative to the diffusive transport of the zinc species.